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The Structure of Ta_3N_5 at 16K by Time-of-Flight Neutron Diffraction

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Abstract:

Polycrystalline Ta_3N_5 has been prepared from the reaction of $TaCl_5$ with ammonia, and its structure has been refined from time-of-flight neutron diffraction data. M_r = 612.88, orthorhombic, *Cmcm*, a = 3.8862(1) Å, b = 10.2118(2) Å, c = 10.2624(3) Å, V = 407.26(3) Å^3, D_x = 9.99 g cm^{-3}, neutron time-of-flight, Rietveld refinement, wR_p, R_p, reduced $\chi 2$ = 0.061, 0.043, 4.21 for data collected at 16 K. Ta_3N_5 crystallizes with the pseudobrookite (Fe_2TiO_5) structure. Irregular TaN_6 octahedra share edges and corners.

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Introduction:

Several authors have mapped out the phase diagram of the Ta-N system (Brauer & Zapp, 1954; Schönberg, 1954b). γ-Ta_2N crystallizes with close-packed metal atoms; the nitrogen atoms fill the octahedral sites. ε-TaN has the *B*35 structure-type which consists of very densely packed metal atoms; nitrogen atoms fill deformed octahedral holes (Brauer & Zapp, 1953; Christensen & Lebech, 1978). Ta_4N_5 and Ta_5N_6 can be prepared as thin films and have been analyzed by electron diffraction (Terao, 1971). At elevated temperatures, δ'-TaN_x forms with the rocksalt structure (Gatterer, Dufek, Ettmayer & Kieffer, 1975). Thin films of δ-$TaN_{0.8-0.9}$ are reported with the hexagonal WC structure (Brauer & Mohr-Rosenbaum, 1971). Some of these interstitial nitrides are probably contaminated with traces of oxygen and carbon.

The nitrides of most interest to us are the fully-nitrided, stoichiometric ones. TaON forms with the baddelyite (ZrO_2) structure in which Ta atoms are irregularly 7-coordinated; oxygen and nitrogen are regularly 3- and 4-coordinated (Armytage & Fender, 1974; Brauer, Weidlein & Strähle, 1966; Weishaupt & Strähle, 1977). The compounds $MTaN_2$ (M=K,Rb,Cs) form with Ta in 4-coordination in the filled β-cristobalite structure, while $NaTaN_2$ forms

with Ta in 6-coordination in the α-$NaFeO_2$ structure (Jacobs & Pinkowski, 1989).

The binary compound, the vermillion Ta_3N_5, has been known for many years (Moureu & Hamblet, 1937). It is reported to have the pseudobrookite (Fe_2TiO_5) structure. Although the unit cell was originally given as metrically tetragonal (Brauer & Weidlein, 1965), its structure has been refined as orthorhombic (Strähle, 1973) and monoclinic (Terao, 1977). If it were truly isomorphic with high-temperature Ti_3O_5 (Åsbrink & Magnéli, 1959), Ta_3N_5 would be monoclinic. The reported structure also contains an unusually short Ta...Ta distance for a compound in which Ta-Ta bonding is not expected so that, in view of the uncertainty about the space group, we felt that it warranted further investigation. We report here neutron diffraction studies which confirm and refine Strähle's orthorhombic structure.

Experimental:

$TaCl_5$ was heated under flowing ammonia gas; the gas had been purified as the liquid over sodium. The temperature was slowly increased to 750°C where a rapid conversion to Ta_3N_5 occurred. The air-stable, maroon-colored material was ground under acetone. X-ray diffraction indicated the presence of

single-phased Ta_3N_5. The details of the synthesis will be published elsewhere (Rauch & DiSalvo, 1991).

Pulsed neutron diffraction data were collected at 16 K on the Neutron Powder Diffractometer (NPD) of the Manuel Lujan, Jr. Neutron Scattering Center at Los Alamos National Laboratory. The powder data were refined with use of the General Structure Analysis System (GSAS), a Rietveld profile analysis code which minimizes $\Sigma w(I_O-I_C)^2$ (Larson & Von Dreele, 1990). Data from the four highest-resolution detector banks (±148°, ±90°) were used which provided 6295 reflections in the range $0.42 < d < 4.0$ Å (27920 profile points). The scattering lengths used were 6.91 and 9.30 x 10^{-15} m for Ta and N, respectively. The 99 variables refined included scale factors, 12 background coefficients for each bank used in a cosine Fourier series technique, 4 profile coefficients for each bank (β_0, β_1, σ_1, σ_2) (Von Dreele, Jorgensen & Windsor, 1982), 2 absorption coefficients (one for each ±bank pair) (Hewat, 1979; Rouse, Cooper & Chakera, 1970), diffractometer zero constants, lattice parameters and 26 modelling parameters. The refinement converged; the structural results are given in Tables I and II. An examination of *R*-values against parity class revealed no unusual trends. The strongest peak on a final difference Fourier synthesis was 0.8% the height of a nitrogen atom (the strongest scatterer). A representative diffraction profile is displayed in Figure 1.

Discussion:

Our structure determination confirms and refines that proposed by Strähle (1973). Terao suggested a similar structural model but proposed the spacegroup *C2/m* (Terao, 1977) based on analogy with Ti_3O_5 at high temperature (Åsbrink & Magnéli, 1959). We transformed our orthorhombic model to the monoclinic setting and found that an unstable refinement in *C2/m* was not statistically better than the refinement in *Cmcm*: the difference profile curve was identical, and the structural parameters did not move more than 1-2 standard deviations away from those of the starting model. We therefore conclude that if Ta_3N_5 is actually monoclinic it is too close to orthorhombic to discern.

The structure of Ta_3N_5 is composed of octahedra of nitrogen atoms centered by tantalum atoms. Since the nitrogen atoms are both 3- and 4-coordinated, the octahedra are irregular. The bond lengths are given in Table III. Both Ta atoms have six Ta...Ta contacts shorter than 3.8 Å (the next-nearest neighbor distance). Figure 2 displays the structure projected on [100].

Shortest Ta-Ta distances derived from oxide and oxynitride materials are typically 3.3 Å, although compounds in which metal-metal bonding might be expected contain

shorter distances (e.g. Ta_4SiTe_4 2.98Å). Shortest Ta-Ta distances for some structures are tabulated in Table IV. The structure for Ta_3N_5 proposed by Strähle, which we confirm, contains a short Ta(2)-Ta(2) distance of 3.00 Å, although the other Ta-Ta distances are over 3.25 Å.

Bond valence parameters appropriate for metal-metal bonding have recently been derived (O'Keeffe & Brese, 1991). These predict the length of a Ta-Ta single bond to be R = 2.78 Å and using the expression (Brown & Altermatt, 1985) for the valence v of a bond of length d: $v = \exp[(R - d)/0.37Å]$, the short bond in Ta_3N_5 corresponds to a valence of 0.55. Note, however, that in a material such as MgO (where the Mg...Mg distance is shorter than in elemental Mg), each of the twelve closest "bonds" is calculated to have a valence of 0.3, although it is generally accepted that there is no metal-metal bonding in this case.

Electrostatic potentials (ϕ) reported in Table I are calculated assuming integral nonoverlapping spherical charges (Tosi, 1964). Since the potential at both Ta sites are similar, both metal atoms are equivalently surrounded by opposite charges. Therefore, based on bond-valence as well as Madelung potential calculations, we believe the close Ta...Ta distance is more a constraint of the pseudobrookite structure than a result of metal-metal bonding.

This material is based upon work supported under a US National Science Foundation Graduate Fellowship to NEB and is part of a continuing program in crystal chemistry supported by the NSF (DMR 8813524). We have benefitted from the use of facilities at the Manuel Lujan, Jr. Neutron Scattering Center, a national user facility, funded as such, by the DOE/Office of Basic Energy Sciences. The synthesis work at Cornell is supported by the Office of Naval Research.

Table I. Structure of Ta_3N_5 at 16K[a]

Atom	Site	*x*	*y*	*z*	$100U_{eqv}$	ϕ(V)
Ta(1)	4*c*	0	0.1971(1)	1/4	0.56	-54.7
			[0.19757(5)		0.37]	
Ta(2)	8*f*	0	0.13455(7)	0.55906(7)	0.60	-54.0
			[0.13429(4)	0.56010(5)	0.37]	
N(3)	4*c*	0	0.76322(7)	1/4	0.85	37.3
			[0.763(1)		0.5]	
N(4)	8*f*	0	0.04701(6)	0.11949(5)	1.00	35.5
			[0.0470(8)	0.119(1)	0.5]	
N(5)	8*f*	0	0.30862(6)	0.07378(5)	0.83	38.5
			[0.3097(9)	0.073(1)	0.4]	

[a]Spacegroup Cmcm, This study: a = 3.88617(9), b = 10.2118(2), c = 10.2624(3); room-temperature study in brackets (Strähle, 1973): a = 3.893, b = c = 10.264. U_{eqv} is defined as 1/3 the trace of the anisotropic temperature coefficients.

Table II. Anisotropic Temperature Factors for Ta_3N_5 at 16K[a]

Atom	$100U_{11}$	$100U_{22}$	$100U_{33}$	$100U_{23}$
Ta(1)	0.48(3)	0.83(3)	0.37(3)	0
Ta(2)	0.37(2)	0.75(2)	0.69(3)	0.01(2)
N(3)	0.80(3)	0.86(3)	0.88(3)	0
N(4)	1.36(2)	0.81(2)	0.83(2)	-0.08(2)
N(5)	0.70(2)	0.83(2)	0.95(2)	0.12(2)

[a] $U_{12} = U_{13} = 0$

Table III. Bond Distances (Å) and Angles (°) for Ta_3N_5

Ta(1)-2Ta(2)	3.2353(8)	N(3)-Ta(1)-N(3)	141.67(7)
Ta(1)-4Ta(2)	3.2513(7)	N(3)-Ta(1)-N(4)	104.31(2)
Ta(1)-2N(3)	2.0571(5)	N(3)-Ta(1)-N(5)	79.93(3)
Ta(1)-2N(4)	2.035(1)	N(4)-Ta(1)-N(4)	82.30(5)
Ta(1)-2N(5)	2.1372(8)	N(4)-Ta(1)-N(5)	81.05(2)
		N(4)-Ta(1)-N(5)	163.35(5)
Ta(2)-Ta(1)	3.2353(8)	N(5)-Ta(1)-N(5)	115.60(6)
Ta(2)-2Ta(1)	3.2513(7)		
Ta(2)-Ta(2)	3.004(1)	N(3)-Ta(2)-N(4)	99.55(4)
Ta(2)-2Ta(2)	3.287(1)	N(3)-Ta(2)-N(4)	177.96(5)
Ta(2)-N(3)	2.2203(8)	N(3)-Ta(2)-N(5)	78.48(2)
Ta(2)-N(4)	1.9550(8)	N(3)-Ta(2)-N(5)	99.44(3)
Ta(2)-N(4)	2.0388(9)	N(4)-Ta(2)-N(4)	82.49(4)
Ta(2)-2N(5)	2.0335(3)	N(4)-Ta(2)-N(5)	78.52(3)
Ta(2)-N(5)	2.240(1)	N(4)-Ta(2)-N(5)	101.06(3)
		N(4)-Ta(2)-N(5)	104.31(3)
N(3)-2Ta(1)	2.0571(5)	N(4)-Ta(2)-N(5)	161.01(4)
N(3)-2Ta(2)	2.2203(8)	N(5)-Ta(2)-N(5)	79.56(3)
		N(5)-Ta(2)-N(5)	145.70(5)
N(4)-Ta(1)	2.035(1)		
N(4)-Ta(2)	1.9550(8)	Ta(1)-N(3)-Ta(1)	141.67(7)
N(4)-Ta(2)	2.0388(9)	Ta(1)-N(3)-Ta(2)	98.88(1)
		Ta(2)-N(3)-Ta(2)	123.91(5)
N(5)-Ta(1)	2.1372(8)		
N(5)-2Ta(2)	2.0335(3)	Ta(1)-N(4)-Ta(2)	105.14(4)
N(5)-Ta(2)	2.240(1)	Ta(1)-N(4)-Ta(2)	157.34(4)
		Ta(2)-N(4)-Ta(2)	97.51(4)
		Ta(1)-N(5)-Ta(2)	95.28(4)
		Ta(1)-N(5)-Ta(2)	102.41(2)
		Ta(2)-N(5)-Ta(2)	100.44(3)
		Ta(2)-N(5)-Ta(2)	145.70(5)

Table IV. Shortest Ta...Ta Distances in Assorted Materials

Compound	Number	Distance(Å)	Reference
Ta	8	2.86	(Mueller, 1977)
ε-TaN	2	2.91	(Christensen & Lebech, 1978)
Ta_4SiTe_4	8	2.97	(Badding & DiSalvo, 1990)
Ta_2CoN_3	6	2.98	(Schönberg, 1954a)
Ta_5N_6	6	2.99	(Fontbonne & Gilles, 1969)
Ta_3MnN_4	6	3.02	(Schönberg, 1954a)
β-Ta_2N	6	3.03	(Conroy & Christensen, 1977)
Ta_4N_5	6	3.04	(Fontbonne & Gilles, 1969)
δ-TaN	12	3.07	(Gatterer, Dufek, Ettmayer & Kieffer, 1975)
[illegible]TaN_2	6	3.13	(Jacobs & Pinkowski, 1989)
TaON	2	3.23	(Armytage & Fender, 1974)
$RbTaO_3$	3	3.24	(Serafin & Hoppe, 1980)
TaI_5	2	3.31	(Müller, 1979)
$TaTe_2$	4	3.32	(Brown, 1966)
α-TaS_2	6	3.35	(Jellinek, 1962)
$TaBO_4$	4	3.40	(Zaslavskij & Zvincuk, 1953)
Ta_3N_5	1	3.00	This study

Figure legends:

1. Neutron diffraction profile fit for Ta_3N_5 at 16 K (2θ = +148° detector bank). The data points are shown as '+' marks, and the solid line is the calculated profile. The difference curve at the bottom is on the same scale. The background has been subtracted.

2. Projection of the Ta_3N_5 structure on (100). The *b* axis is horizontal, and the *c* axis is vertical. The dark-shaded octahedra are displaced by *a*/2 from the lighter ones. Dark circles represent the 4-coordinated N atoms, while the lighter circles represent the 3-coordinated ones. Larger circles represent Ta atoms within the octahedra.

3. Projection of the Ta_3N_5 structure on (100) emphasizing anion coordination. Larger circles again represent Ta atoms. The edge-sharing tetrahedra are centered by N atoms. The shading of the circles indicates displacement by *a*/2.

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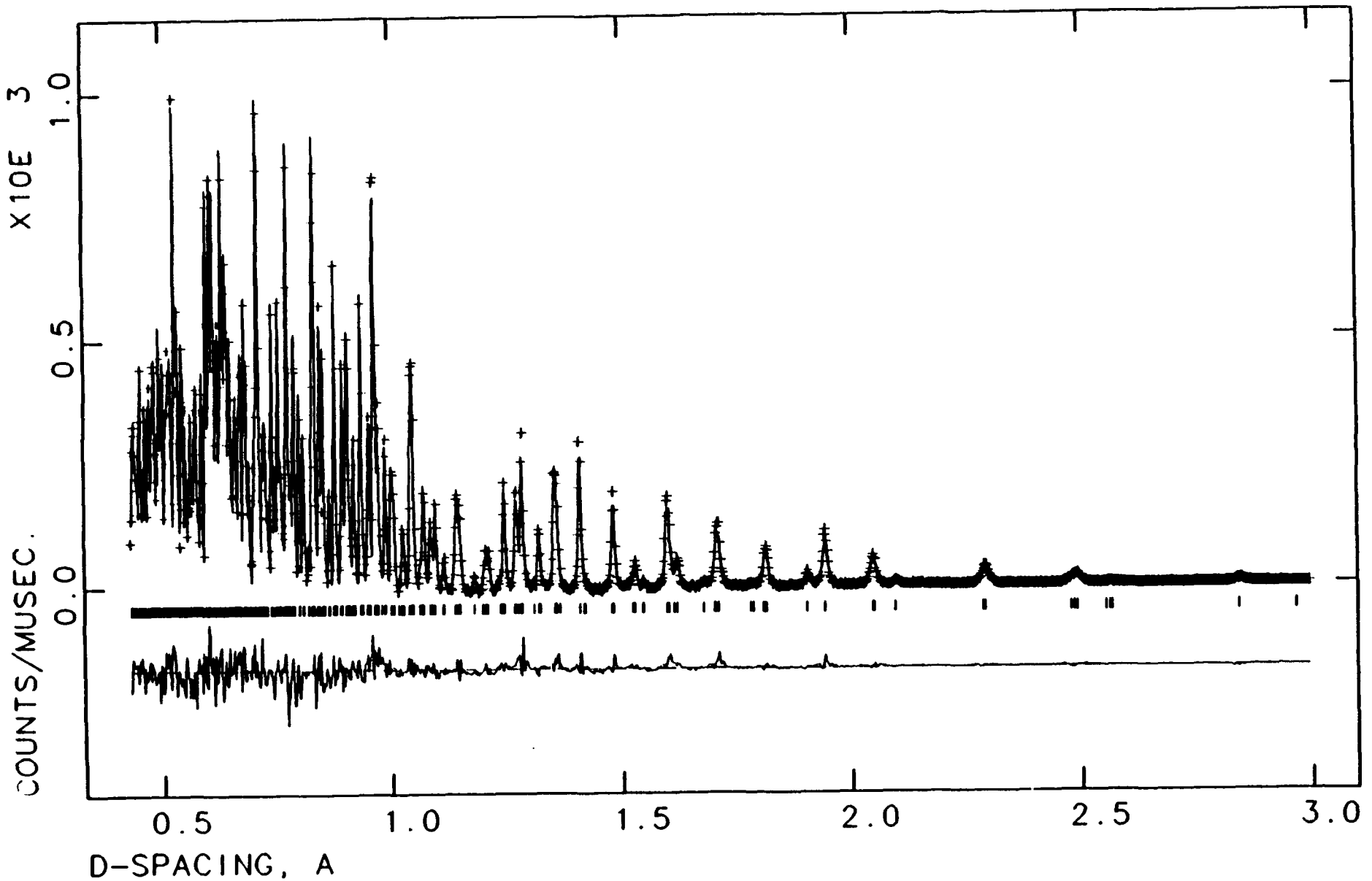

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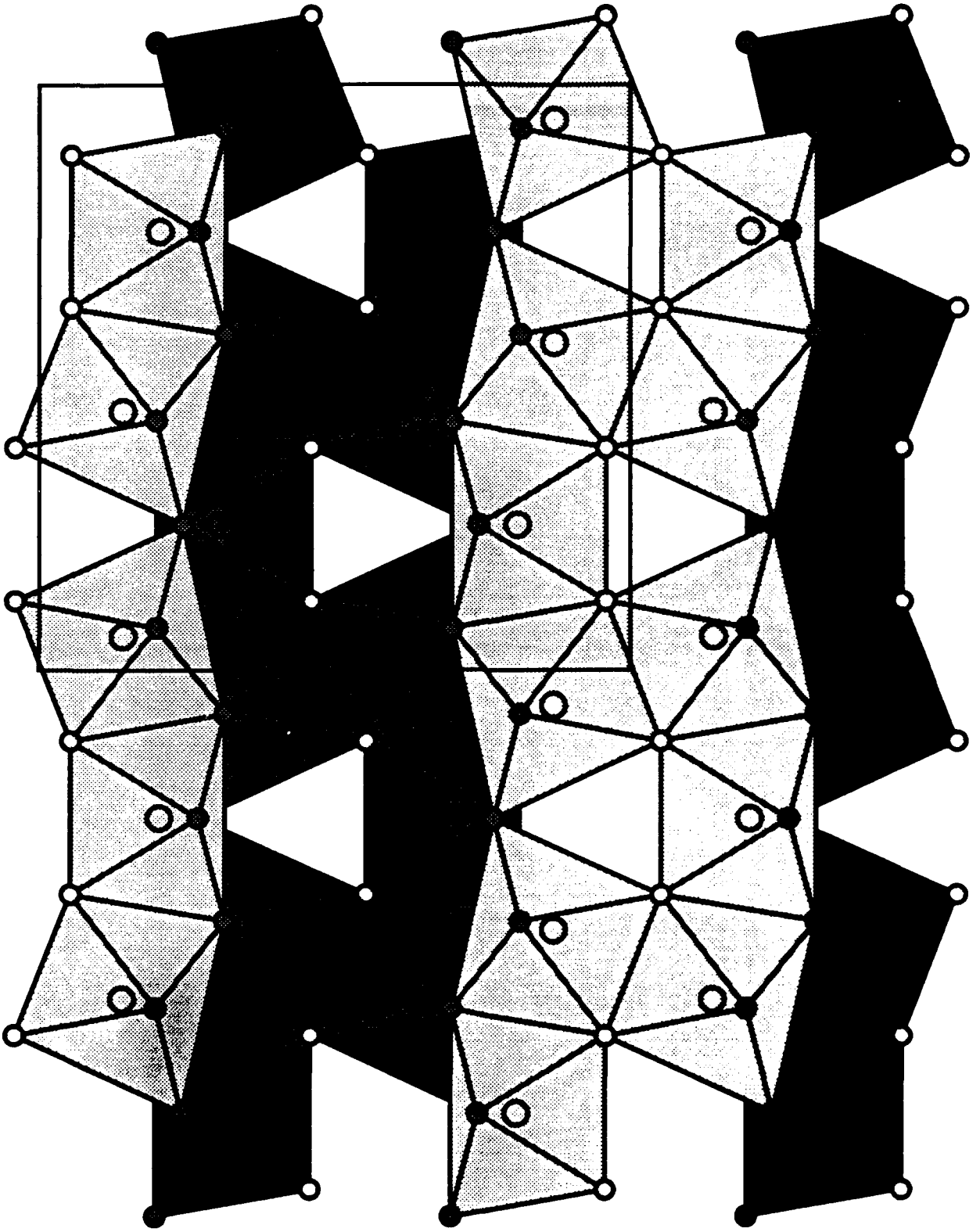

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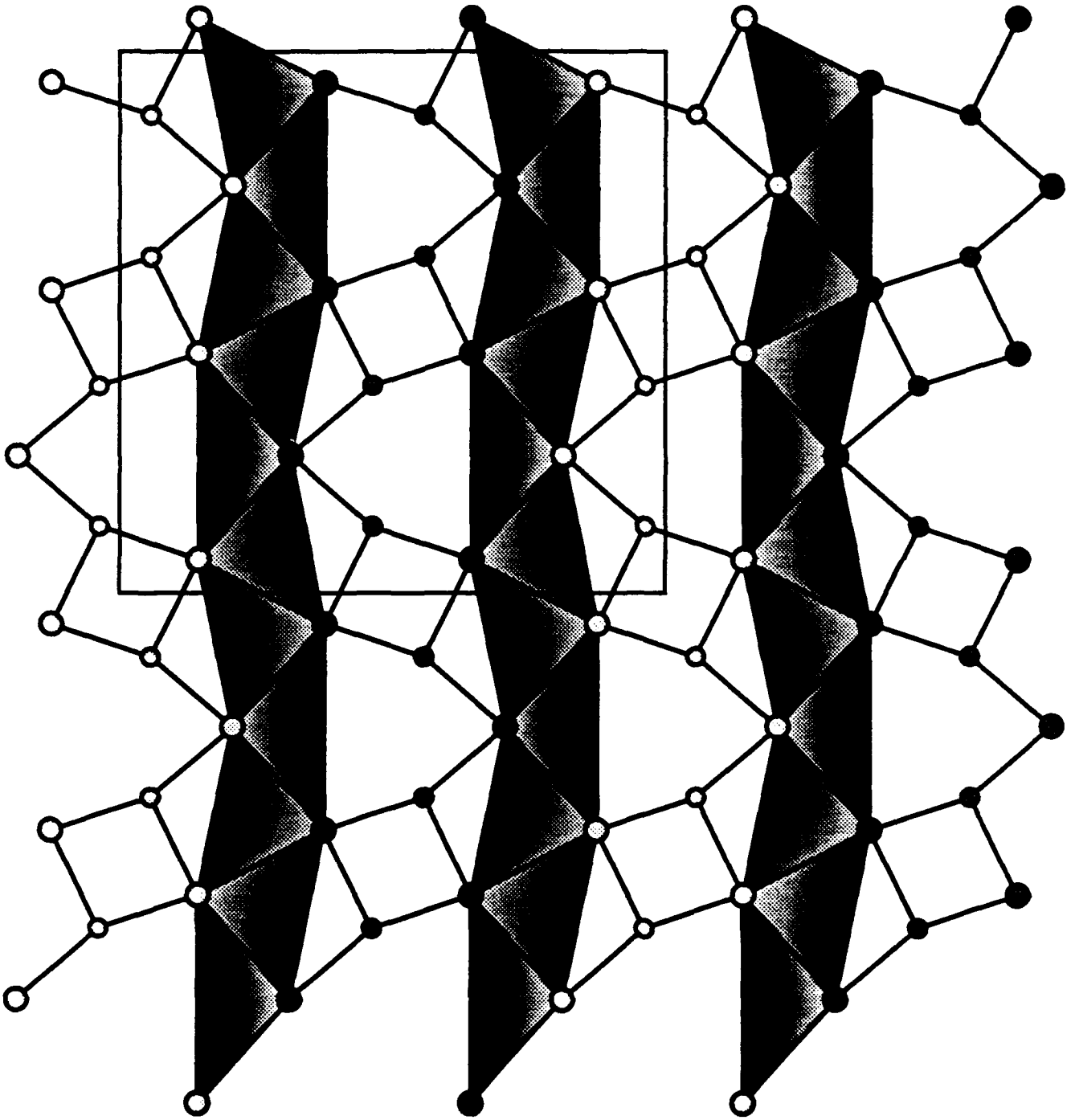

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